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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 9/26, C08L 1/02	A1	(11) International Publication Number: WO 98/28360 (43) International Publication Date: 2 July 1998 (02.07.98)
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(54) Title: CELLULOSE SPONGES (57) Abstract <p>A cellulose sponge is disclosed, which is formed from coagulated cellulose solution having a mean degree of polymerisation (DP) which does not exceed 800. Preferably, the DP lies in the range 450-600. The sponge may be reinforced by discontinuous fibres, preferably of cellulose, and may be treated with a wetting agent or softener. The sponge may also contain one or more surfactants. Water retention may be improved by partial etherification. Also disclosed is a method of manufacture of a cellulose sponge from a solution of cellulose in an amine oxide solvent. Dispersed throughout the solution is an additive (such as a water soluble inorganic salt or a water soluble organic material) which provides sites for the formation of cells within the cellulose solution as it regenerates. A foaming agent or a blowing agent may be employed to assist in cell formation. Natural rubber latex may also be added in order to increase mechanical strength, and in some cases to increase absorbency.</p> <p style="text-align: center;"><i>10 or 2°</i></p>		

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CELLULOSE SPONGES

This invention relates to cellulose sponges and to methods for the manufacture of cellulose sponges.

It is well known to produce sponges from cellulose via the viscose or xanthate process. Such a method of making sponges is described in US-A-3,382,303, and in EP-A-0,670,344.

However, the xanthate process for the manufacture of regenerated cellulose is being superseded by a process in which cellulose articles are formed from a solution of cellulose in an aqueous tertiary amine N-oxide solvent which is regenerated in an aqueous regeneration bath. Such a process is described in US-A-4,246,221, the contents of which are hereby incorporated herein by way of reference.

15 According to the present invention there is provided a cellulose sponge formed from coagulated cellulose solution, the cellulose having a mean degree of polymerisation which does not exceed 800.

Preferably the degree of polymerisation is less than 20 600, and preferably lies in the range 450-600. This provides optimum water retention whilst still maintaining acceptable physical properties for the sponge material.

The sponge may be reinforced by discontinuous fibres, preferably cellulose fibres (for example lyocell, viscose or 25 cotton fibres), having lengths selected from a range of 1 to 10mm. Lyocell fibres having an initial length of 8mm are particularly suitable, with the concentration of fibres being in the range 10-50% by weight, based on the weight of cellulose.

30 Preferably the sponge is treated with a wetting agent or softener, such as polyethylene glycol (PEG), preferably PEG 400.

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Alternatively or additionally the sponge may include a surfactant or a mixture of surfactants, such as a coconut oil grafted with polyethylene glycol and lauric diethanolamide, the surfactant (or mixture) being added to
5 the cellulose solution prior to coagulation.

The water retention of the sponge may also be improved by partial etherification of the cellulose. Preferably the etherification is by way of either carboxymethylation or carboxyethylation.

10 Also according to the invention there is provided a method of manufacture of a cellulose sponge in which a solution of cellulose in an amine oxide solvent is mixed with at least one additive which is dispersed throughout the solution prior to regeneration thereof, the additive
15 providing sites for the formation of cells within the cellulose solution as it regenerates, wherein the degree of polymerisation of the cellulose in solution does not exceed about 800.

Preferably the degree of polymerisation is in the range
20 450-600.

Preferably the additive is a water soluble material that can be washed out of the cellulose solution as it regenerates. The additive can be a water soluble inorganic salt, such as sodium chloride or sodium sulphite. In
25 particular, with sodium chloride, the quantity of additive can be up to 80 times by weight, based on the cellulose in solution. Alternatively, the additive can be a water soluble organic material which is not soluble in the cellulose solution, such as polyethylene glycol (PEG). The
30 soluble organic material may have a molecular weight in the range 1000-4000, preferably in the range 1500-3500, and may be used in quantities of 700%-2000% based on the weight of cellulose.

not necessarily

The cellulose solution may be caused to foam by the use of a chemically activated foaming agent, for example sodium bicarbonate, which may be mixed into the cellulose solution immediately prior to regeneration in amounts in the range 5 50%-500% by weight of cellulose, preferably about 100% to 120% by weight of cellulose.

Citric acid may be added directly to the dope, preferably in an amount in the range 100%-120%, by weight of cellulose. The cellulose dope may be regenerated in an 10 aqueous citric acid solution.

The bicarbonate can be activated in a regeneration bath by the use of 10% by weight of citric acid in solution in the aqueous regeneration bath.

Preferably the bath has a temperature of 40-50°C.

15 A further alternative is the use of a physical blowing agent, such as a gas or volatile liquid, which can be mixed into the cellulose solution under pressure, say in an extruder, and which expands as the solution exits the extruder.

20 Preferably, whilst still wet or in a never dried condition, the cellulose sponge is placed in a solution of a wetting agent, preferably 20% PEG 400, to improve its water retention properties after drying.

Alternatively, whilst still in the wet or never-dried 25 condition, the water retention properties can be improved by boiling the cellulose sponge in a solution of sodium chloride, initially a 10% solution, for 30 minutes and then washing.

The tensile properties of the sponge may be improved by 30 immersing the never-dried sponge in an aqueous emulsion of natural rubber latex and then drying the impregnated sponge.

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The water retention properties of the sponge may be further improved by etherification of the cellulose, preferably by carboxymethylation. The cellulose pulp is subjected to etherification up to a maximum substitution of 5 0.3% before being dissolved in the amine oxide solvent, and then being subjected to the foaming process.

The invention will hereinafter be described in more detail by way of example only, with reference to the following practical examples and tests.

10 Preparation of Cellulose Solution

Cellulose solutions were prepared in 200 g batches, starting from a mixed solvent comprising 80% by weight N-methyl-morpholine-N-oxide (NMMO) and 20% by weight water. The solvent and a desired amount of cellulose pulp were 15 subjected to 10^{-2} mbar (1N.m^{-2}) vacuum and heated to 90°C to 95°C to remove water, so that the solution comprised a desired percentage of cellulose in a mixed solvent comprising approximately 85% by weight NMMO and 15% by weight of water.

20 The mixture was stirred every half hour until no pulp fibre was observed through a 100x optical microscope.

Porosity promoters or foaming agents and reinforcing fibres were added to the cellulose solution immediately prior to casting or extrusion. With the cellulose solution 25 at about 85°C - 95°C , the fibres and additive were mixed in by hand using a spatula and stirring until a homogeneous mixture was obtained.

Regeneration

Each cellulose solution was cast onto a temperature 30 conditioned glass plate to a thickness of 1 mm. The glass plate was then immersed in a regeneration bath containing water at a desired temperature for several hours. The *Coagulation*

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content of the bath was changed regularly to avoid the build up of materials leached into the water.

The regenerated cellulose sponge samples were of varying thickness.

5 Reinforcing Fibre

The reinforcing fibres comprised cotton (2mm), viscose (5mm) and lyocell (10mm). (The fibre lengths are the lengths prior to milling.) The fibres were milled at the fastest speed setting on a Kenwood blender model BL360 for 10 at least one minute until a fluffy pulp was obtained.

Foaming Additives

A number of different additives were added to the cellulose solutions. The additives essentially comprise:-

(a) additives that could be leached out of the regenerating
15 cellulose to produce a cellular structure. These were
essentially (i) inorganic salts having a high
solubility in water, and which are solid at about 85-
90°C, such as sodium chloride and sodium sulphite, and
(ii) organic solids which are insoluble in the
20 cellulose solution at 85-90°C, e.g. polyethylene
glycols (PEG) such as PEG 1500 and PEG 3500, (which
have average molecular weights of 1500 and 3500
respectively);

(b) Chemical blowing agents which can be activated at about
25 20-50°C, for example sodium bicarbonate, which is
activated by the addition of 10% by weight citric acid
to the regeneration bath water held at a selected
temperature.

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Water Holding Capacity

The water holding capacity of the sponge materials was measured as follows:-

Residue water was removed from the regenerated samples
5 by contact with tissue whilst taking care not to squeeze the
sponge. The sample was weighed wet and then left to dry at
ambient temperature for several days until a constant weight
was obtained. Alternatively the samples may be dried at
95°C until a constant weight is obtained. The difference
10 between the wet and dry sample weights divided by the dry
sample weight indicates the percentage water content of a
never-dried sample.

Following drying, the sponges were immersed in water
for at least 24 hours, and preferably for two days, and then
15 weighed as before. The difference between the wet sample
weight and the dry mass of the sponge, divided by the dry
weight indicates the percentage water content on rewetting.

Softening or Wetting Agents

A selection of samples of cellulose sponge were soaked
20 for 24 hours in 20% solution of PEG 400 in water and then
dried at room temperature and rewetted. Their subsequent
water retention capacities were compared with those of
never-dried sponges and of dried sponges without the PEG 400
treatment.

25 The invention will now be illustrated by way of
example, with reference to the Examples given below.

The effect of regeneration temperature and degree of
polymerisation is shown below in Table A.

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TABLE A

Example	Pulp	Bath Temp. °C	% Water never dried	% Water dried-rewet	B/A
			A	B	
A-1	13% LV	20	149	60	0.4
A-2	13% LV	20	197	56	0.28
A-3	13% LV	120	406	124	0.31
A-4	10%LV/HV	50	411	116	0.28
A-5	10%LV/HV	50	619	108	0.17
A-6	7% LV/HV	20	921	207	0.22
A-7	7% LV	20	1009	110	0.11
A-8	7% LV	50	1205	136	0.11

15 LV = cellulose having a mean Degree of Polymerisation (DP) of about 485

LV/HV = cellulose having a mean Degree of Polymerisation of 600

Note Sample 3 was regenerated in steam.

20 From the Examples in Table 'A' it can be seen that as the regeneration bath temperature is increased to 50°C, the porosity of the cellulose increases (see samples A-1 and A-2 compared with sample A-3, and sample A-8 compared with samples A-6 and A-7).

25 Furthermore, as the concentration of cellulose in the solution decreases, the porosity increases (see samples A-1 and A-7), and as the degree of polymerisation decreases the capacity for water retention of the cellulose increases.

The Formation of Sponges using Leaching Techniques

Further cellulose sponge samples were produced and tested, as shown in Table B below:

TABLE B

Examples	Pulp	Bath Temp °C	Additive	Lyocell Reinforcement	% Water never dried	% Water dried - rewet
B - 1	5% LV/HV	50	420% NMMO	56%	870	66
B - 2	10% LV	50	1000% Na ₂ SO ₄		995	127
B - 3	7% LV/HV	50	1500% NaCl		1470	
B - 3a	6% LV/HV	20	8000% NaCl		2080	800
B - 4	5% LV/HV	50	700% PEG	28%	718	124
B - 5	5% LV/HV	50	1400% PEG	28%	940	183
B - 6	5% LV/HV	50	1400% PEG		1040	140
B - 7	7% LV/HV	25	1500% PEG		1270	220
B - 8	5% LV/HV	40	1500% PEG	50%	1660	242
B - 9	2% LV/HV	50	1750% PEG		1820	257

If a sponge is arbitrarily defined as a porous material which can hold approximately 1000% or more of its weight of water then it can be seen from samples B-2 or B-3 that sponges can be formed using inorganic salts. It was observed that the cellulose solution tended to dry on addition of huge amounts of inorganic salts. In particular, the mixture of cellulose dope with sodium chloride in Example 3a produced a dough formed in a ½ cm thick slab which was regenerated in cold water (at room temperature of about 20°C) for 3 hours. Hot water, e.g. 50°C, was found to be unsuitable. For complete regeneration and leaching out of the sodium chloride the microporous sponge was boiled in hot water for about 1 hour. The resultant sponge had high water retention.

All PEG samples were made using 1500 mw PEG except for B-5, where 3500 mw PEG was used. It was observed that the greater the volume of PEG added in the cellulose solution, the greater the void volume generated in the sponge.

It was found that the upper limit of PEG that could be added to the cellulose solution was about 1800% by weight with fibre reinforcement present. The reduction in the cellulose content of the solution aided the inclusion of the 5 larger volumes of PEG. The lower molecular weight PEG is more effective at creating pores than the high molecular weight PEG (see B-5 and B-6).

The preferred sample B-9 was able to retain a significant amount of water, up to approximately 1800%, in 10 the never-dried state.

The Use of Bicarbonate Foaming Agents

Table C below illustrates the results of tests of further cellulose sponges, manufactured using a bicarbonate foaming agent:

TABLE C

<u>Example</u>	<u>Pulp</u>	<u>Bath Temp. °C</u>	<u>Bicarb -onate %</u>	<u>Reinforcer</u>	<u>% Water never dried</u>	<u>% Water dried-rewet</u>
					<u>A</u>	<u>B</u>
C-1	13% LV	50	100		615	101
C-2	13% LV	50	200		677	122
C-3	10% LV	20	100		680	123
C-4	10% LV	50	100		731	122
C-5	7% LV/HV	20	100		820	88
C-6	7% LV/HV	50	100	28% cotton	830	134
C-7	7% LV/HV	20	100	28% viscose	930	206
C-8	7% LV/HV	20	100	28% cotton	1000	138
C-9	3% LV/HV	50	117	210% lyocell	1100	200
C-10	3% LV/HV	50	47	117% lyocell	1150	108
C-11	7% LV	20	100		1156	138
C-12	7% LV/HV	50	100		1170	
C-13	3% LV/HV	50	70	117% lyocell	1250	176
C-14	7% LV	50	100		1282	156
C-15	7% LV/HV	50	100	28% viscose	1380	91
C-16	3% LV/HV	50	117	117% lyocell	1460	214
C-17	7% LV	50	100		1609	270
C-18	3% LV/HV	30	466	70% lyocell	2200	120
C-19	3% LV/HV	50	117	47% lyocell	2289	183
C-20	10% LV/HV	40	200	20% lyocell	1215	329

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Generally, the more bicarbonate added to the cellulose solution the greater the water retention, up to an addition of about 120% by weight of cellulose (C-10, C-13, C-16). Above about 120% the cellulose foam structure tended to collapse. A regeneration bath temperature of about 50°C was found to be beneficial.

The greater void volumes are produced when the bicarbonate is used in combination with reinforcing fibres (see C-5, C-7 and C-8).

10 Good porosity of the sponge depends on a balance being struck between the cellulose content of the solution, the reinforcing fibre content, and the amount of bicarbonate present. For example, the presence of excess fibres hinders the foaming process. Sample C-19 produced optimum porosity
15 with a relatively small amount of both bicarbonate and reinforcing fibres. The higher the cellulose content in solution the better the percentage water retention on rewetting.

Water Softener or Wetting Agent Application

20 Various samples from Tables B and C were tested for the effect of a 20% PEG wash upon their water retention properties, and the results are set out in Table D below:

TABLE D

Example	% Water Never-dried	% Water Dried-Rewetted (20% PEG wash)	% Water Dried-rewet Without PEG
B-1	870	520 (60%)	65 (7%)
B-6	1040	690 (66%)	140 (13%)
B-7	1270	1040 (82%)	220 (17%)
B-9	1820	1650 (91%)	255 (14%)
C-13	1250	1060 (85%)	175 (14%)
C-16	1460	940 (64%)	215 (15%)
C-19	2290	1515 (66%)	185 (8%)

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(The figures in brackets denote the percentage water content of the never dried product).

The subsequent water retention capacities of the sponges treated within PEG were found to be greatly increased compared with the dried-rewet capacities of the original sponges. However, the effect of the wetting agent was observed to deteriorate with subsequent washing.

Etherification

The cellulose was partially derivatised to give partial Carboxymethyl Cellulose (CMC) substitution.

Method of Carboxymethylation

Blended LV and HV Viscokraft pulps with a mean DP of 600 were treated with a solution of sodium hydroxide and stirred for 40 minutes to form the 'alkcell'. To this, a solution of sodium monochloroacetate (SMCA) in water was added. Low substitution levels were obtained by slowing the reaction rate by jacketing the reaction vessel with iced water. After a time samples were neutralised with very dilute hydrochloric acid. Water was used for washing, being removed by wringing the samples in a muslin sheet. The dry samples were submitted for a sulphate ash test to determine the degree of substitution (DS). Conditions for obtaining a particular DS are tabulated in the Table E below for reactions on 50g of LV/HV pulp.

25 **TABLE E. Carboxymethylation Reaction Conditions**

CMC DS	Time (mins)	Temp. °C	% NaOH cm ³	% SMCA cm ³
0.016	40	5	30 250	30 250
0.021	60	5	20 250	20 250
0.035	120	5	30 250	30 250
0.046	180	5	30 250	30 250
0.059	2	110	50 250	50 250
0.136	10	110	saturated 250	saturated 250
0.214	20	110	saturated 250	saturated 250
0.295	30	110	saturated 250	saturated 250

Formation of CMC Sponges

7% cellulose solutions or dopes were prepared, using the above carboxymethylated samples, in the manner previously discussed on page 4.

5 The cellulose dope at 95°C was then mixed with 100% citric acid (based on weight of cellulose) and allowed to stand for 5 minutes. It has been found that the addition of citric acid to the dope improves the water retention of the sponges. 100% sodium bicarbonate and 28% by weight of
10 viscose fibres were then added to the dope which was allowed to rest for a further 5 minutes. The activated dope was then cast onto a glass surface to form a sponge pad after regeneration. The sponges were formed by regeneration in 10% aqueous citric acid solution at 50°C. This is very similar
15 to sample C-15.

The water retention properties of the CMC sponges are given in Table F.

TABLE F. Sponges from Carboxylated Cellulose

SAMPLE	Degree of Substitution by Carboxymethyl	% Water 'never-dried' A	% Water dried-rewetted B	% 'Never-dried' recovered B/A
F-1	0.016	1800	320	18
F-2	0.021	1460	270	19
F-3	0.035	1600	310	19
F-4	0.046	2050	450	22
F-5	0.059	2370	400	17
F-6	0.136	2480	635	26
F-7	0.214	2765	580	21
F-8	0.295	2450	560	23

30 It can be seen that as more cellulose hydroxyl groups are substituted by carboxymethyl groups, up to substitution levels of 0.136/0.214, the water retention capacity increases of both the never-dried and dried sponge.

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Substitution levels beyond 0.136 gave no further improvement to the water capacity of dried sponges.

Post Regeneration Treatment with Latex

Sponges made according to Sample F-6 were allowed to dry to around 500% water content. They were then immersed in solutions of between 0.1 and 4% natural latex in water. With no further washing the sponges were dried completely in an oven at 95°C.

The latex coated sponges were tested for water retention and the results are given in Table G below:-

TABLE G. Latex-coated Sponges

% Latex on Sponge	% Water Dried-rewetted
0	635
0.11	560
0.29	597
0.36	605
0.46	686
0.55	702
0.88	483
1.4	304

Natural rubber latex solution applied to a formed sponge is dried using heat such that it coalesces into a flexible and resilient film on the cellulose surface. Latex has a strong affinity for hydrophilic surfaces and the low viscosity of solutions allows penetration into the thick sponge structures. Since latex does not become brittle or shrink even in dry environments, it helps maintain sponge porosity.

Latex was applied to the partially dried sponges (~500% water) so that they swelled. Latex solutions of between 0.6 and 8% solids concentration were used. The weight of latex absorbed by the sponges was observed to be approximately one

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fifth of the latex bath concentration, eg a bath of 2.4% solids gave a sponge with 0.55% latex by weight of cellulose.

The greater the level of latex deposited in the sponge, from 0.11 to 0.55%, the greater is the sponge capacity for 5 water after drying, up to about 700%. However the presence of latex at concentrations below 0.35% is detrimental in comparison to the sponge with no latex applied. Improvement in the sponge by applying 0.55% latex is only ~10%. Increasing further the concentration of latex applied creates a poor 10 never-dried product.

By using latex a small increase in absorbency may be achieved, but real advantages are likely to be increased mechanical strengths and wear resistance.

Post-regeneration Treatment with Sodium Chloride

15 Never-dried sponges made as for samples F-3, F-4, F-7 and F-8 were immersed in a solution of sodium chloride (10%) and boiled for 30 minutes. The rate of evaporation was such that the salt eventually saturated the solution such that solid sodium chloride was visible. Without washing the sponge 20 further it was dried at 95°C. The sample was weighed, then washed thoroughly to remove the residual salt.

 Samples impregnated with salt were subjected to two drying/washing cycles. The first cycle was used to measure the amount of salt absorbed and the second wash to remove the 25 residual salt before drying again. This second cycle was used to generate the 'dried-rewetting' figure.

 The water retention of the salt-treated samples was then measured and the results are given in Table H below.

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TABLE H. Salt Treated Sponges

	% Water 'never- dried' A	% Water dried- rewetted B	% Never- dried recovered d B/A	% Salt after 1st dry
CMC 0.046DS boiled	2050	470	23	0
0.035DS boil in NaCl	1645	860	52	200
0.046DS boil in NaCl	2150	1051	50	200
0.214DS boil in NaCl	2765	1120	40	150
0.295DS boil in NaCl	2450	810	33	150

After boiling in saturated salt solution the sponges changed very little in appearance and volume through the drying and rewetting cycles. They maintained up to 52% of their never-dried capacity for water, and in two cases gave 15 over 1000% water on dried-rewetted cellulose.

Addition of Oils and Fatty Acids to the Cellulose Dope

Lauric diethanolamine (15% by weight of cellulose) and coconut oil with a grafted polyethylene glycol 600 (50% by weight of cellulose) were stirred into a 7% LV/HV cellulose 20 dope similar to sample C-15 at 95°C. The dope was then treated with sodium bicarbonate as described above in relation to the manufacture of CMC sponges.

The resulting sample was compared with a similar sample dope prepared without any additive present.

25 Long chain additives are entrapped into the cellulose structure giving a permanent disrupting effect between cellulose chains. The treated sponge was not particularly porous, holding only 1215% its weight of water, as compared with about 1700% for the untreated sample. The water 30 absorption is possibly hindered by the waxy nature of the additives. The treated sponge had improved absorbency after drying, retaining 27% of the 'never-dried' capacity (324% water); as compared with 17% for the untreated sample.

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CLAIMS

1. A cellulose sponge formed from coagulated cellulose solution, the cellulose having a mean degree of polymerisation (DP) which does not exceed 800.

5 2. A sponge as claimed in claim 1 wherein the mean DP is less than 600.

3. A sponge as claimed in claim 1 or claim 2 wherein the cellulose has undergone etherification with a maximum degree of substitution of 0.36%.

10 4. A sponge as claimed in claim 3 wherein the cellulose sponge has undergone carboxymethylation.

5. A sponge as claimed in any one of claims 1 to 4, further including up to 0.6% by weight of natural rubber latex dispersed throughout the sponge.

15 6. A sponge as claimed in any one of claims 1 to 5, further including a fibre reinforcement.

7. A sponge as claimed in claim 6 wherein the fibre reinforcement is provided by lyocell fibres.

8. A sponge as claimed in claim 6 or claim 7 wherein
20 ~~the reinforcing fibre content does not exceed 50% by weight~~
of the cellulose.

9. A sponge as claimed in any one of claims 1 to 8, further including a surfactant and/or wetting agent.

10. A sponge as claimed in claim 9, further including
25 a wetting agent additive comprising polyethylene glycol or a substituted polyethylene glycol.

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11. A cellulose sponge comprising cellulose which has undergone etherification with a maximum degree of substitution of 0.3%.

12. A method of manufacture of a cellulose sponge in which a solution of cellulose in an amine oxide solvent is mixed with at least one additive which is dispersed throughout the solution prior to regeneration thereof, the additive providing sites for the formation of cells within the cellulose solution as it is regenerated, wherein the degree of polymerisation of the cellulose in solution does not exceed about 800.

13. A method as claimed in claim 12 wherein said at least one additive is a water-soluble material which can be leached out of the cellulose solution in an aqueous regeneration bath.

14. A method as claimed in claim 13 wherein the water-soluble material is a hydrated inorganic solid.

15. A method as claimed in claim 14 wherein the inorganic salt comprises sodium chloride added in an amount of up to 80 times by weight on cellulose to form a dough which is subsequently regenerated in water at about 20°C.

16. A method as claimed in claim 13 wherein the soluble material is a polyethylene glycol (PEG).

17. A method as claimed in claim 16 wherein the PEG has a molecular weight of between 1500 and 3500.

18. A method as claimed in claim 17 wherein the maximum weight of PEG added to the cellulose solution is about 1800% by weight of cellulose.

19. A method as claimed in claim 12 wherein said additive is a chemically reactive agent which is activated by heat or by the regeneration bath.

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20. A method as claimed in claim 19 wherein the additive is a bicarbonate which is activated by the presence of acid within the dope and/or the regeneration bath.

21. A method as claimed in claim 19 or claim 20
5 wherein the additive comprises a mixture of sodium bicarbonate and citric acid.

22. A method as claimed in claim 20 or claim 21 wherein the regeneration bath includes citric acid in solution.

23. A method as claimed in claim 12 wherein the
10 additive is a fluid which is mixed into the solution under pressure and which volatizes or expands on the release of pressure in the regeneration bath to form a sponge.

24. A method as claimed in claim 23 wherein the fluid is an organic liquid.

15 25. A method as claimed in any one of claims 12 to 24 in which reinforcing fibres are added to the solution.

26. A method as claimed in any one of claims 12 to 25 wherein a fatty acid compound is added to the dope prior to regeneration.

20 27. A method as claimed in any one of claims 16 to 26 wherein the never-dried sponge after regeneration is boiled in a saturated solution of sodium chloride, and washed.

28. A method as claimed in any one of claims 12 to 27 wherein the never-dried sponge is immersed after regeneration
25 in an aqueous emulsion of natural latex, and dried.

29. A method as claimed in any one of claims 12 to 28 in which a polyethylene glycol softener is applied to the cellulose sponge after regeneration but prior to drying.

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30. A method of manufacture as claimed in any one of claims 12 to 29 wherein the cellulose is subjected to etherification with a maximum substitution of 0.3% before being dissolved in the amine oxide solvent.

5 31. A method of manufacture of a cellulose sponge in which a solution of cellulose in amine oxide is mixed with at least one additive which is dispersed throughout the solution prior to regeneration thereof and which provides sites for the formation of cells within the cellulose solution as it is
10 regenerated, wherein the cellulose is subjected to etherification with a maximum substitution of 0.3% before being dissolved in the amine oxide solvent.

32. A method of etherification of cellulose solution in an amine oxide solvent wherein the cellulose pulp undergoes
15 etherification with a maximum substitution of 0.3% before being dissolved in the amine oxide solvent.

33. A method of manufacture of a cellulose moulding in which the cellulose has been subjected to etherification by a method as claimed in claim 32.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 97/03534

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08J 9/26, C08L 1/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08J, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 9742259 A1 (FINANCIERE ELYSEES BALZAC), 13 November 1997 (13.11.97), claims 1, 2 and 9; abstract; page 3, line 16 - line 17	1-2,12
P,A	WO 9723552 A1 (LENZING AKTIENGESELLSCHAFT), 3 July 1997 (03.07.97), claims 1 and 15; abstract	1,12
A	EP 0418151 A1 (FINANCIERE ELYSEES BALZAC), 20 March 1991 (20.03.91)	1-33
A	EP 0670344 A1 (NISSHINBO INDUSTRIES, INC.), 6 Sept 1995 (06.09.95)	1-33

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 March 1998

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

Date of mailing of the international search report

22 04 1998

Authorized officer

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 97/03534

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3382303 A (F. B. STIEG), 7 May 1968 (07.05.68) ----- -----	1-33

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/GB 97/03534

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WO	9723552	A1	03/07/97	AT	210095 A	15/02/97
				AT	402932 B	25/09/97
				AU	1132697 A	17/07/97
				CA	2213234 A	03/07/97
				EP	0811031 A	10/12/97
				NO	973762 A	15/08/97
EP	0418151	A1	20/03/91	CA	2025035 A	13/03/91
				FR	2651783 A,B	15/03/91
EP	0670344	A1	06/09/95	JP	7242767 A	19/09/95
US	3382303	A	07/05/68	NONE		